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CLAIMS

[Claim(s)]
[Claim 1] The manufacture method of the hydrogen-storing-metal-alloy electrode which carries out the reduction processing of the aforementioned hydrogen-storing-metal-alloy powder after the aforementioned rinsing and dryness, and is characterized by to mix with the aforementioned thickener or a binder after that in the manufacture method of the hydrogen-storing-metal-alloy electrode which puts the paste which was mixed with the thickener or the binder and formed the hydrogen-storing-metal-alloy powder rinsed and dried after processing with either [at least] an acid or alkali on a metal charge collector, and forms it.
[Claim 2] The manufacture method of the hydrogen-storing-metal-alloy electrode characterized by to carry out the reduction processing of the aforementioned hydrogen-storing-metal-alloy electrode which put the aforementioned paste on the aforementioned metal charge collector, and was formed in the manufacture method of the hydrogen-storing-metal-alloy electrode which puts the paste which was mixed with the thickener or the binder and formed the hydrogen-storing-metal-alloy powder rinsed and dried on a metal charge collector, and forms it after processing with either [at least] an acid or alkali.
[Claim 3] In the manufacture method of the hydrogen storing metal alloy electrode which puts the paste which was mixed with the thickener or the binder and formed the hydrogen storing metal alloy powder rinsed and dried after processing with either [at least] an acid or alkali on a metal charge collector, and forms it The manufacture method of the hydrogen storing metal alloy electrode characterized by carrying out reduction processing of the aforementioned hydrogen storing metal alloy electrode which put the aforementioned paste on the aforementioned metal charge collector, and was formed while mixing with the aforementioned thickener or a binder, after carrying out reduction processing of the aforementioned hydrogen storing metal alloy powder after the aforementioned rinsing and dryness.
[Claim 4] For the aforementioned reduction processing, 3 is [the claim 1 performed using hydrogen peroxide solution, or] the manufacture method of the hydrogen storing metal alloy electrode a publication either.
[Claim 5] For the aforementioned reduction processing, 3 is [the claim 1 performed using elevated-temperature hydrogen gas or] the manufacture method of the hydrogen storing metal alloy electrode a publication either.

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Translation of 09-63573

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to an improvement of the initial-activity-ized property in detail about the manufacture method of a hydrogen storing metal alloy electrode.
[0002]
[Description of the Prior Art] Performing nickel plating and copper coating to hydrogen storing metal alloy powder, and raising the initial-activity-ized property of a hydrogen storing metal alloy electrode, a cycle life, internal conductivity, etc. conventionally, in the manufacture method of the hydrogen storing metal alloy electrode which puts the paste which was mixed with the binder and formed hydrogen storing metal alloy powder on a metal charge collector, and forms it, is proposed.
[0003] Moreover, removing misch metals, such as easy-oxidizable La which projects on a hydrogen storing metal alloy powder front face according to acid treatment or an alkali treatment, and the oxide of those, forming a nickel rich layer in the surface section of hydrogen storing metal alloy powder, and acquiring the same effect as the above-mentioned nickel plating before mixture with a binder, is also proposed. For example, JP,3-152868,A processes hydrogen storing metal alloy powder in acid solution before binder mixture. It proposes processing with an alkaline-water solution and improving an initial-activity-ized property. then, JP,5-101821,A It proposes processing hydrogen storing metal alloy powder with an elevated-temperature alkaline-water solution, and improving an initial-activity-ized property before binder mixture. JP,5-13077,A It has proposed processing again the hydrogen storing metal alloy electrode formed using the hydrogen storing metal alloy powder processed with the elevated-temperature alkaline-water solution with an elevated-temperature alkaline-water solution, and improving an initial-activity-ized property.
[0004]
[Problem(s) to be Solved by the Invention] However, although the oxide of a misch metal with which the above-mentioned acid treatment and the alkali treatment were formed in the front face of hydrogen storing metal alloy powder was removed, the surface oxide film or surface hydroxylation film of a nickel rich layer (nickel) could not fully be removed, but there was fault of degrading the initial-activity-ized property of a hydrogen storing metal alloy electrode,

internal conductivity, etc.
[0005] this invention is made paying attention to the above-mentioned viewpoint, and it is making to offer the manufacture method of the hydrogen storing metal alloy electrode which improved an initial-activity-ized property and internal conductivity into the technical problem which should be solved.
[0006]
[A The means for solving a technical problem and an effect of the invention] The 1st composition of this invention is the manufacture method of the hydrogen-storing-metal-alloy electrode which carries out [mixing the aforementioned hydrogen-storing-metal-alloy powder with the aforementioned thickener or a binder, after carrying out reduction processing, and] as the feature after the aforementioned rinsing and dryness in the manufacture method of the hydrogen-storing-metal-alloy electrode which puts the paste which was mixed with the thickener or the binder and formed the hydrogen-storing-metal-alloy powder rinsed and dried on a metal charge collector, and forms it after processing with either [at least] an acid or alkali.
[0007] According to this composition, it can have the property which is easy to dissolve in oxidization or alkali, and the oxide of the misch metal projected from the surface nickel layer of hydrogen storing metal alloy powder etc. can be removed after acid treatment or an alkali treatment. Furthermore, by these acid treatment or the alkali treatment, the surface nickel oxide film and surface nickel hydroxylation film of a nickel rich layer which have not fully been removed are removable with subsequent reduction processing. For this reason, the reactivity and conductivity of hydrogen storing metal alloy powder can improve, and the initial-activity-ized property of a hydrogen storing metal alloy electrode and conductivity can be improved.
[0008] In addition, with an example of the conventional hydrogen-absorption rechargeable battery, it supposes that 1 charge-and-discharge cycle is completed in 10 hours, and 7, then time (duration to about 95% of capacity realization of maximum capacity) required for initial-activity-izing cannot turn into 70 hours, and power required for it cannot disregard the number of cycles required for initial-activity-izing, either, but the improvement in an initial-activity-ized property has the important meaning from productivity or the point of improvement in a manufacturing facility utilization factor.
[0009] It is the manufacture method of the hydrogen-storing-metal-alloy electrode which carries out [that it carries out the reduction processing of the aforementioned hydrogen-storing-metal-alloy electrode which put the aforementioned paste on the aforementioned metal charge collector, and was formed in the manufacture method of the hydrogen-storing-metal-alloy electrode which puts the paste which was mixed with the thickener or the binder and formed the hydrogen-storing-metal-alloy powder rinsed and dried on a metal charge collector, and forms it after processing the 2nd composition of this invention with either / at least / an acid or alkali, and] as the feature. Since the nickel oxide film which will be formed in the front face of hydrogen storing metal alloy powder by the time it forms an electrode after carrying out reduction processing in the 1st composition of the above since reduction processing of the hydrogen storing metal alloy electrode is carried out can also be returned according to this invention, an effect can be improved further.
[0010] After processing the 3rd composition of this invention with either [at least] an acid or alkali further in the above 1st and the 2nd composition, In the manufacture method of the hydrogen storing metal alloy electrode which puts the paste which was mixed with the thickener

or the binder and formed the hydrogen storing metal alloy powder rinsed and dried on a metal charge collector, and forms it After the aforementioned rinsing and dryness, after carrying out reduction processing of the aforementioned hydrogen storing metal alloy powder, while mixing with the aforementioned thickener or a binder, it is characterized by carrying out reduction processing of the aforementioned hydrogen storing metal alloy electrode which put the aforementioned paste on the aforementioned metal charge collector, and was formed. Since reduction processing is performed doubly according to this invention, the above-mentioned operation effect can be improved further.

[0011] The 4th composition of this invention is further characterized by performing the aforementioned reduction processing using hydrogen peroxide solution in the above 1st or one composition of the 3rd. Hydrogen peroxide solution does not have the need mentioned above of washing by a lot of wash waters after that like acid treatment or an alkali treatment, and is easy on a process. The 5th composition of this invention is further characterized by performing the aforementioned reduction processing using elevated-temperature hydrogen gas in the above 1st or one composition of the 3rd. Since elevated-temperature hydrogen gas does not need subsequent backwashing by water like the acid treatment mentioned above or an alkali treatment, it is easy.

[0012]

[The gestalt which invents] The suitable mode of this invention is explained based on the following examples.

[0013]

[Example] Hereafter, each example of the manufacture method of the hydrogen storing metal alloy electrode of this invention is explained.

(Example 1) the hydrogen storing metal alloy powder which composition carried out machine trituration of the hydrogen storing metal alloy which is MmNi3.6 Co0.75aluminum0.3 Mn0.35 (La/Mm=0.6), and made 150 or less meshes -- the inside of 680-degree C NKOH solution -- 24 hours -- being immersed -- an alloy front face -- alkali etching -- carrying out -- after after that, rinsing, and dryness (inside of air), and CMC(carboxymethyl cellulose)2wt% solution -- an alloy weight -- receiving -- 20wt(s)% -- in addition, it stirred and the

[0014] Next, the foaming nickel charge collector (10cmx10cm and 550 g/m2) was filled up with this paste, it dried at 70-80 degrees C, and thickness was set to 0.6mm in the roll press. Next, it rinsed and this electrode was dried, after being under 30wt% hydrogen peroxide solution for 3 hours. The obtained hydrogen storing metal alloy electrode was pinched through separator on the sintering formula nickel pole of a couple, it was immersed in 6NKOH solution, ten cells (example article) of negative-electrode regulation were produced, it charged by 0.1C on the basis of negative-electrode geometric capacity after that for 10.5 hours, and the charge-and-discharge cycle made to discharge to 0.8V by 0.1C was carried out after that for activation. Furthermore, similarly ten example articles of comparison which merely omitted only being immersed [hydrogen peroxide solution] by the manufacturing process same as an example of comparison as the above-mentioned example article were produced. The measurement result of the number of charge-and-discharge cycles at this time and a capacity utilization factor (ratio of actual capacity to negative-electrode geometric capacity) is shown in drawing 1 . In drawing 1 , with a circle [white] shows the average of an example article, and a black dot shows the average of the example article of comparison. it turns out that it is markedly alike from drawing 1 with

reduction processing, and an initial-activity-ized property can be improved
(Example 2) Next, three hydrogen storing metal alloy electrodes produced in the example 1 were pinched through separator on the sintering formula nickel pole of four sheets, respectively, ten pieces were constituted by having used the square shape sealing cell as the example article, it charged by 0.1C for 10.5 hours on the basis of positive-electrode geometric capacity (100% of negative-electrode geometric capacity), and the charge-and-discharge cycle made to discharge to 1.0V by 0.1C was carried out after that for activation. Ten example articles of comparison which merely used the hydrogen storing metal alloy electrode as the example article of comparison of an example 1 with this composition were produced, and the cell internal pressure at those charge end time was measured. The average (white round head) of the cell internal pressure of each example article and the average (black dot) of the cell internal pressure of each example article of comparison are shown in drawing 2 . it turns out that it is markedly alike from drawing 2 with reduction processing, and cell internal pressure can be reduced
[0015] in addition, it is common knowledge that cell internal pressure has strong negative correlation to the cycle life of a cell, and it is presumed that the cycle life of this example article is markedly alike, and can improve from drawing 2
(Example 3) Ten example articles which it was immersed into 30-degree C 1-N formic acid solution instead of the alkali etching in the above-mentioned example 1 for 24 hours, and acid etching of the alloy front face was carried out, and also were produced at the same process as an example 1 were produced, it charged by 0.1C on the basis of negative-electrode geometric capacity after that for 10.5 hours, and the charge-and-discharge cycle made to discharge to 0.8V by 0.1C was carried out after that for activation. Furthermore, similarly ten example articles of comparison which merely omitted only being immersed [hydrogen peroxide solution] by the manufacturing process same as an example of comparison as the above-mentioned example article were produced. The measurement result of the number of charge-and-discharge cycles at this time and a capacity utilization factor (ratio of actual capacity to negative-electrode geometric capacity) is shown in drawing 3 . In drawing 3 , with a circle [white] shows the average of an example article, and a black dot shows the average of the example article of comparison. it turns out that it is markedly alike from drawing 3 with reduction processing, and an initial-activity-ized property can be improved
(Example 4) Next, three hydrogen storing metal alloy electrodes produced in the example 3 were pinched through separator on the sintering formula nickel pole of four sheets, respectively, ten pieces were constituted by having used the square shape sealing cell as the example article, it charged by 0.1C for 10.5 hours on the basis of positive-electrode geometric capacity (100% of negative-electrode geometric capacity), and the charge-and-discharge cycle made to discharge to 1.0V by 0.1C was carried out after that for activation. Ten example articles of comparison which merely used the hydrogen storing metal alloy electrode as the example article of comparison of an example 3 with this composition were produced, and the cell internal pressure at those charge end time was measured. The average (white round head) of the cell internal pressure of each example article and the average (black dot) of the cell internal pressure of each example article of comparison are shown in drawing 4 . it turns out that it is markedly alike from drawing 4 with reduction processing, and cell internal pressure can be reduced
(Example 5) Composition was immersed into 680-degree C NKOH solution for 24 hours in the hydrogen storing metal alloy powder which carried out machine trituration of the hydrogen

storing metal alloy which is MmNi3.6 Co0.75aluminum0.3 Mn0.35 (La/Mm=0.6), and was made into 150 or less meshes, carried out alkali etching of the alloy front face, and rinsed and dried after that (inside of air). Next, it rinsed and this hydrogen storing metal alloy powder was dried, after being under 30wt% hydrogen peroxide solution for 3 hours. next, CMC2wt% solution -- an alloy weight -- receiving -- 20wt(s)% -- in addition, it stirred and the paste was formed Next, the foaming nickel charge collector (10cmx10cm and 550 g/m2) was filled up with this paste, it dried at 70-80 degrees C, and thickness was set to 0.6mm in the roll press.

[0016] The obtained hydrogen storing metal alloy electrode was pinched through separator on the sintering formula nickel pole of a couple, it was immersed in 6NKOH solution, ten cells (example article) of negative-electrode regulation were produced, it charged by 0.1C on the basis of negative-electrode geometric capacity after that for 10.5 hours, and the charge-and-discharge cycle made to discharge to 0.8V by 0.1C was carried out after that for activation. Furthermore, similarly ten example articles of comparison which merely omitted only being immersed [hydrogen peroxide solution] by the manufacturing process same as an example of comparison as the above-mentioned example article were produced. The measurement result of the number of charge-and-discharge cycles at this time and a capacity utilization factor (ratio of actual capacity to negative-electrode geometric capacity) is shown in drawing 5 . In drawing 5 , with a circle [white] shows the average of an example article, and a black dot shows the average of the example article of comparison. it turns out that it is markedly alike from drawing 5 with reduction processing, and an initial-activity-ized property can be improved

(Example 6) Next, three hydrogen storing metal alloy electrodes produced in the example 5 were pinched through separator on the sintering formula nickel pole of four sheets, respectively, ten pieces were constituted by having used the square shape sealing cell as the example article, it charged by 0.1C for 10.5 hours on the basis of positive-electrode geometric capacity (100% of negative-electrode geometric capacity), and the charge-and-discharge cycle made to discharge to 1.0V by 0.1C was carried out after that for activation. Ten example articles of comparison which merely used the hydrogen storing metal alloy electrode as the example article of comparison of an example 1 with this composition were produced, and the cell internal pressure at those charge end time was measured. The average (white round head) of the cell internal pressure of each example article and the average (black dot) of the cell internal pressure of each example article of comparison are shown in drawing 6 . it turns out that it is markedly alike from drawing 6 with reduction processing, and cell internal pressure can be reduced

(Example 7) Ten example articles which it was immersed into 30-degree C 1-N formic acid solution instead of the alkali etching in the above-mentioned example 5 for 24 hours, and acid etching of the alloy front face was carried out, and also were produced at the same process as an example 5 were produced, it charged by 0.1C on the basis of negative-electrode geometric capacity after that for 10.5 hours, and the charge-and-discharge cycle made to discharge to 0.8V by 0.1C was carried out after that for activation. Furthermore, similarly ten example articles of comparison which merely omitted only being immersed [hydrogen peroxide solution] by the manufacturing process same as an example of comparison as the above-mentioned example article were produced. The measurement result of the number of charge-and-discharge cycles at this time and a capacity utilization factor (ratio of actual capacity to negative-electrode geometric capacity) is shown in drawing 7 . In drawing 7 , with a circle [white] shows the average of an example article, and a black dot shows the average of the example article of comparison. it turns

out that it is markedly alike from drawing 7 with reduction processing, and an initial-activity-ized property can be improved
(Example 8) Next, three hydrogen storing metal alloy electrodes produced in the example 7 were pinched through separator on the sintering formula nickel pole of four sheets, respectively, ten pieces were constituted by having used the square shape sealing cell as the example article, it charged by 0.1C for 10.5 hours on the basis of positive-electrode geometric capacity (100% of negative-electrode geometric capacity), and the charge-and-discharge cycle made to discharge to 1.0V by 0.1C was carried out after that for activation. Ten example articles of comparison which merely used the hydrogen storing metal alloy electrode as the example article of comparison of an example 3 with this composition were produced, and the cell internal pressure at those charge end time was measured. The average (white round head) of the cell internal pressure of each example article and the average (black dot) of the cell internal pressure of each example article of comparison are shown in drawing 8 . it turns out that it is markedly alike from drawing 8 with reduction processing, and cell internal pressure can be reduced
(Example 9) As compared with each above-mentioned examples 1-6, what held reduction processing for 1 hour and performed it to elevated-temperature hydrogen gas (suitably 300-600 degrees C, pressures 0.1-1 MPa) in atmosphere instead of being immersed [hydrogen peroxide solution] was produced. These hydrogen storing metal alloy electrodes showed the capacity utilization factor property almost equal to a hydrogen storing metal alloy electrode and cell internal pressure property of the above-mentioned examples 1-5. It turns out that the reducing agent used for reduction processing from this fact is not limited to hydrogen peroxide solution.

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(54) **MANUFACTURE OF HYDROGEN STORAGE ALLOY ELECTRODE**

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a manufacturing process of a hydrogen storage alloy electrode with high initial activation characteristics and high internal conductivity.

SOLUTION: Oxide of misch metal attached onto the surface nickel layer of hydrogen storage alloy powder, having a property easily soluble to a acid or an alkali is removed by acid treatment or alkali treatment. A nickel oxide film or a nickel hydroxide film, which was not yet sufficiently removed by the acid treatment or the alkali treatment on the surface of a nickel rich layer is removed by reduction treatment. The reactivity and conductivity of the hydrogen storage alloy powder are enhanced, and the initial activation characteristics and the conductivity of a hydrogen storage alloy electrode are enhanced.

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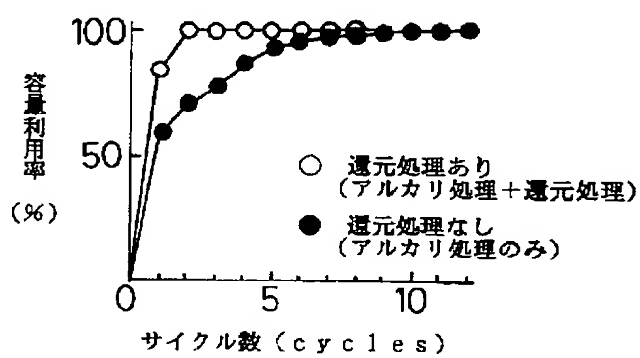
(54)【発明の名称】　水素吸蔵合金電極の製造方法

(57)【要約】
【課題】初期活性化特性や内部導電性を向上した水素吸蔵合金電極の製造方法を提供すること。
【解決手段及び発明の効果】酸又はアルカリに溶解しやすい性質をもち、水素吸蔵合金粉末の表面ニッケル層しているミッシュメタルの酸化物などを酸処理又はアルカリ処理後で除去し、更にその後の還元処理により、これら酸処理又はアルカリ処理では充分に除去できなかったニッケルリッチ層の表面のニッケル酸化膜やニッケル水酸化膜を除去する。このため水素吸蔵合金粉末の反応性や導電性が向上し、水素吸蔵合金電極の初期活性化特性や導電性を向上することができる。



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【特許請求の範囲】

【請求項１】酸及びアルカリの少なくとも一方で処理した後、水洗、乾燥した水素吸蔵合金粉末を増粘剤又は結着剤と混合して形成したペーストを金属集電体に被着して形成する水素吸蔵合金電極の製造方法において、
前記水洗、乾燥後、前記水素吸蔵合金粉末を還元処理し、その後、前記増粘剤又は結着剤と混合することを特徴とする水素吸蔵合金電極の製造方法。

【請求項２】酸及びアルカリの少なくとも一方で処理した後、水洗、乾燥した水素吸蔵合金粉末を増粘剤又は結着剤と混合して形成したペーストを金属集電体に被着して形成する水素吸蔵合金電極の製造方法において、
前記ペーストを前記金属集電体に被着して形成された前記水素吸蔵合金電極を還元処理することを特徴とする水素吸蔵合金電極の製造方法。

【請求項３】酸及びアルカリの少なくとも一方で処理した後、水洗、乾燥した水素吸蔵合金粉末を増粘剤又は結着剤と混合して形成したペーストを金属集電体に被着して形成する水素吸蔵合金電極の製造方法において、
前記水洗、乾燥後、前記水素吸蔵合金粉末を還元処理した後、前記増粘剤又は結着剤と混合するとともに、前記ペーストを前記金属集電体に被着して形成された前記水素吸蔵合金電極を還元処理することを特徴とする水素吸蔵合金電極の製造方法。

【請求項４】前記還元処理は過酸化水素水を用いて行われる請求項１乃至３のいずれか記載の水素吸蔵合金電極の製造方法。

【請求項５】前記還元処理は高温水素ガスを用いて行われる請求項１乃至３のいずれか記載の水素吸蔵合金電極の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、水素吸蔵合金電極の製造方法に関し、詳しくはその初期活性化特性の改善に関する。

【０００２】

【従来の技術】従来、水素吸蔵合金粉末を結着剤と混合して形成したペーストを金属集電体に被着して形成する水素吸蔵合金電極の製造方法において、水素吸蔵合金粉末にニッケルメッキや銅メッキを施して水素吸蔵合金電極の初期活性化特性やサイクル寿命や内部導電性などを向上させることが提案されている。

【０００３】また、結着剤との混合前に、酸処理やアルカリ処理により水素吸蔵合金粉末表面に突出する易酸化性のＬａなどのミッシュメタルやその酸化物を除去して、水素吸蔵合金粉末の表面部にニッケルリッチ層を形成して上記ニッケルメッキと同様の効果を得ることも提案されている。例えば特開平３－１５２８６８号公報は、結着剤混合前に水素吸蔵合金粉末を酸性水溶液で処理し、その後、アルカリ水溶液で処理して初期活性化特性を改善することを提案し、特開平５－１０１８２１号公報は、結着剤混合前に水素吸蔵合金粉末を高温アルカリ水溶液で処理して初期活性化特性を改善することを提案し、特開平５－１３０７７号公報は、高温アルカリ水溶液で処理した水素吸蔵合金粉末を用いて形成した水素吸蔵合金電極を再度、高温アルカリ水溶液で処理して初期活性化特性を改善することを提案している。

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【０００４】

【発明が解決しようとする課題】しかしながら、上記した酸処理やアルカリ処理は水素吸蔵合金粉末の表面に形成されたミッシュメタルの酸化物は除去するが、ニッケルリッチ層（ニッケル）の表面の酸化膜や水酸化膜を充分に除去できず、水素吸蔵合金電極の初期活性化特性や内部導電性などを劣化させるという不具合があった。

【０００５】本発明は上記観点に着目してなされたものであり、初期活性化特性や内部導電性を向上した水素吸蔵合金電極の製造方法を提供することを、その解決すべき課題としている。

【０００６】

【課題を解決するための手段及び発明の効果】本発明の第１の構成は、酸及びアルカリの少なくとも一方で処理した後、水洗、乾燥した水素吸蔵合金粉末を増粘剤又は結着剤と混合して形成したペーストを金属集電体に被着して形成する水素吸蔵合金電極の製造方法において、前記水洗、乾燥後、前記水素吸蔵合金粉末を還元処理した後、前記増粘剤又は結着剤と混合することを特徴とする水素吸蔵合金電極の製造方法である。

【０００７】本構成によれば、酸化又はアルカリに溶解しやすい性質をもち、水素吸蔵合金粉末の表面ニッケル層から突出しているミッシュメタルの酸化物などを酸処理又はアルカリ処理後で除去することができる。更にその後の還元処理により、これら酸処理又はアルカリ処理では充分に除去できなかったニッケルリッチ層の表面のニッケル酸化膜やニッケル水酸化膜を除去できる。このため水素吸蔵合金粉末の反応性や導電性が向上し、水素吸蔵合金電極の初期活性化特性や導電性を向上することができる。

【０００８】なお、従来の水素吸蔵二次電池の一例では、１充放電サイクルを１０時間で完了するとし、初期活性化に必要なサイクル数を７とすれば、初期活性化に必要な時間（最大容量の９５％程度の容量実現までの所要時間）は７０時間となり、それに必要な電力も無視することができず、初期活性化特性の向上は生産性や製造設備利用率の向上の点から重要な意味を有している。

【０００９】本発明の第２の構成は、酸及びアルカリの少なくとも一方で処理した後、水洗、乾燥した水素吸蔵合金粉末を増粘剤又は結着剤と混合して形成したペーストを金属集電体に被着して形成する水素吸蔵合金電極の製造方法において、前記ペーストを前記金属集電体に被着して形成された前記水素吸蔵合金電極を還元処理する

ことを特徴とする水素吸蔵合金電極の製造方法である。本発明によれば、水素吸蔵合金電極を還元処理するので、上記第１の構成において還元処理した後、電極を形成するまでに水素吸蔵合金粉末の表面に形成されるニッケル酸化膜も還元することができるので、効果を一層向上することができる。

【００１０】本発明の第３の構成は、上記第１及び第２の構成において更に、酸及びアルカリの少なくとも一方で処理した後、水洗、乾燥した水素吸蔵合金粉末を増粘剤又は結着剤と混合して形成したペーストを金属集電体に被着して形成する水素吸蔵合金電極の製造方法において、前記水洗、乾燥後、前記水素吸蔵合金粉末を還元処理した後、前記増粘剤又は結着剤と混合するとともに、前記ペーストを前記金属集電体に被着して形成された前記水素吸蔵合金電極を還元処理することを特徴としている。本発明によれば還元処理を二重に行うので上記作用効果を一層向上することができる。

【００１１】本発明の第４の構成は、上記第１乃至第３のいずれかの構成において更に、前記還元処理を過酸化水素水を用いて行うことを特徴としている。過酸化水素水は上述した酸処理やアルカリ処理のようにその後に多量の洗浄水で洗浄する必要が無く工程上簡単である。本発明の第５の構成は、上記第１乃至第３のいずれかの構成において更に、前記還元処理を高温水素ガスを用いて行うことを特徴としている。高温水素ガスは上述した酸処理やアルカリ処理のようなその後の水洗浄を必要としないので簡単である。

【００１２】

【発明を実施する形態】本発明の好適な態様を以下の実施例に基づいて説明する。

【００１３】

【実施例】以下、本発明の水素吸蔵合金電極の製造方法の各実施例を説明する。

（実施例１）組成が$MmNi_{3.6}Co_{0.75}Al_{0.3}Mn_{0.35}$（Ｌａ／Ｍｍ＝０．６）である水素吸蔵合金を機械粉砕して１５０メッシュ以下とした水素吸蔵合金粉末を８０℃の６ＮＫＯＨ水溶液中に２４時間浸漬して合金表面をアルカリエッチングし、その後、水洗、乾燥（空気中）後、ＣＭＣ（カルボキシメチルセルロース）２ｗｔ％水溶液を合金重量に対して２０ｗｔ％加えて撹拌し、ペーストを形成した。

【００１４】次に、このペーストを発泡ニッケル集電体（１０ｃｍ×１０ｃｍ、５５０ｇ／ｍ^2）に充填し、７０～８０℃で乾燥し、ロールプレスにて厚さを０．６ｍｍにした。次に、この電極を３０ｗｔ％過酸化水素水に３時間浸漬した後、水洗、乾燥した。得られた水素吸蔵合金電極をセパレータを介して一対の焼結式ニッケル極で挟持し、６ＮＫＯＨ水溶液に浸漬して負極規制の電池（実施例品）を１０個作製し、その後、負極理論容量を基準として０．１Ｃで１０．５時間充電し、その後、０．１Ｃで０．８Ｖまで放電させる充放電サイクルを活性化処理のために実施した。更に、比較例として上記実施例品と同じ製造工程でただ過酸化水素水への浸漬だけを省略した比較例品を同じく１０個作製した。この時の充放電サイクル数と容量利用率（負極理論容量に対する実際容量の比）との測定結果を図１に示す。図１において、実施例品の平均値を白丸で示し、比較例品の平均値を黒丸で示す。図１から還元処理により格段に初期活性化特性を向上できることがわかる。

（実施例２）次に、実施例１で作製した水素吸蔵合金電極３枚をそれぞれセパレータを介して４枚の焼結式ニッケル極で挟んで角型密閉電池を実施例品として１０個構成し、正極理論容量（負極理論容量の１００％）を基準として０．１Ｃで１０．５時間充電し、その後、０．１Ｃで１．０Ｖまで放電させる充放電サイクルを活性化処理のために実施した。同構成でただ水素吸蔵合金電極を実施例１の比較例品とした比較例品１０個を作製し、それらの充電終了時点における電池内圧を測定した。各実施例品の電池内圧の平均値（白丸）と各比較例品の電池内圧の平均値（黒丸）とを図２に示す。図２から還元処理により格段に電池内圧を低減できることがわかる。

【００１５】なお、電池内圧は電池のサイクル寿命に対して強く負の相関を有することが周知であり、図２から本実施例品のサイクル寿命が格段に改善できることが推定される。

（実施例３）上記実施例１におけるアルカリエッチングの代わりに３０℃の１Ｎ蟻酸水溶液中に２４時間浸漬して合金表面を酸エッチングした他は、実施例１と同じ工程で作製した実施例品を１０個作製し、その後、負極理論容量を基準として０．１Ｃで１０．５時間充電し、その後、０．１Ｃで０．８Ｖまで放電させる充放電サイクルを活性化処理のために実施した。更に、比較例として上記実施例品と同じ製造工程でただ過酸化水素水への浸漬だけを省略した比較例品を同じく１０個作製した。この時の充放電サイクル数と容量利用率（負極理論容量に対する実際容量の比）との測定結果を図３に示す。図３において、実施例品の平均値を白丸で示し、比較例品の平均値を黒丸で示す。図３から還元処理により格段に初期活性化特性を向上できることがわかる。

（実施例４）次に、実施例３で作製した水素吸蔵合金電極３枚をそれぞれセパレータを介して４枚の焼結式ニッケル極で挟んで角型密閉電池を実施例品として１０個構成し、正極理論容量（負極理論容量の１００％）を基準として０．１Ｃで１０．５時間充電し、その後、０．１Ｃで１．０Ｖまで放電させる充放電サイクルを活性化処理のために実施した。同構成でただ水素吸蔵合金電極を実施例３の比較例品とした比較例品１０個を作製し、それらの充電終了時点における電池内圧を測定した。各実施例品の電池内圧の平均値（白丸）と各比較例品の電池内圧の平均値（黒丸）とを図４に示す。図４から還元処

理により格段に電池内圧を低減できることがわかる。

（実施例５）組成が$MmNi_{3.6}Co_{0.75}Al_{0.3}Mn_{0.35}$（Ｌａ／Ｍｍ＝０．６）である水素吸蔵合金を機械粉砕して１５０メッシュ以下とした水素吸蔵合金粉末を８０℃の６ＮＫＯＨ水溶液中に２４時間浸漬して合金表面をアルカリエッチングし、その後、水洗、乾燥（空気中）した。次に、この水素吸蔵合金粉末を３０ｗｔ％過酸化水素水に３時間浸漬した後、水洗、乾燥した。次に、ＣＭＣ２ｗｔ％水溶液を合金重量に対して２０ｗｔ％加えて攪拌し、ペーストを形成した。次に、このペーストを発泡ニッケル集電体（１０ｃｍ×１０ｃｍ、５５０ｇ／ｍ^2）に充填し、７０～８０℃で乾燥し、ロールプレスにて厚さを０．６mmにした。

【００１６】得られた水素吸蔵合金電極をセパレータを介して一対の焼結式ニッケル極で挟持し、６ＮＫＯＨ水溶液に浸漬して負極規制の電池（実施例品）を１０個作製し、その後、負極理論容量を基準として０．１Ｃで１０．５時間充電し、その後、０．１Ｃで０．８Ｖまで放電させる充放電サイクルを活性化処理のために実施した。更に、比較例として上記実施例品と同じ製造工程でただ過酸化水素水への浸漬だけを省略した比較例品を同じく１０個作製した。この時の充放電サイクル数と容量利用率（負極理論容量に対する実際容量の比）との測定結果を図５に示す。図５において、実施例品の平均値を白丸で示し、比較例品の平均値を黒丸で示す。図５から還元処理により格段に初期活性化特性を向上できることがわかる。

（実施例６）次に、実施例５で作製した水素吸蔵合金電極３枚をそれぞれセパレータを介して４枚の焼結式ニッケル極で挟んで角型密閉電池を実施例品として１０個構成し、正極理論容量（負極理論容量の１００％）を基準として０．１Ｃで１０．５時間充電し、その後、０．１Ｃで１．０Ｖまで放電させる充放電サイクルを活性化処理のために実施した。同構成でただ水素吸蔵合金電極を実施例１の比較例品とした比較例品１０個を作製し、それらの充電終了時点における電池内圧を測定した。各実施例品の電池内圧の平均値（白丸）と各比較例品の電池内圧の平均値（黒丸）とを図６に示す。図６から還元処理により格段に電池内圧を低減できることがわかる。

（実施例７）上記実施例５におけるアルカリエッチングの代わりに３０℃の１Ｎ蟻酸水溶液中に２４時間浸漬して合金表面を酸エッチングした他は、実施例５と同じ工程で作製した実施例品を１０個作製し、その後、負極理論容量を基準として０．１Ｃで１０．５時間充電し、その後、０．１Ｃで０．８Ｖまで放電させる充放電サイクルを活性化処理のために実施した。更に、比較例として上記実施例品と同じ製造工程でただ過酸化水素水への浸漬だけを省略した比較例品を同じく１０個作製した。この時の充放電サイクル数と容量利用率（負極理論容量に対する実際容量の比）との測定結果を図７に示す。図７において、実施例品の平均値を白丸で示し、比較例品の平均値を黒丸で示す。図７から還元処理により格段に初期活性化特性を向上できることがわかる。

（実施例８）次に、実施例７で作製した水素吸蔵合金電極３枚をそれぞれセパレータを介して４枚の焼結式ニッケル極で挟んで角型密閉電池を実施例品として１０個構成し、正極理論容量（負極理論容量の１００％）を基準として０．１Ｃで１０．５時間充電し、その後、０．１Ｃで１．０Ｖまで放電させる充放電サイクルを活性化処理のために実施した。同構成でただ水素吸蔵合金電極を実施例３の比較例品とした比較例品１０個を作製し、それらの充電終了時点における電池内圧を測定した。各実施例品の電池内圧の平均値（白丸）と各比較例品の電池内圧の平均値（黒丸）とを図８に示す。図８から還元処理により格段に電池内圧を低減できることがわかる。

（実施例９）上記各実施例１～６に比較して還元処理を過酸化水素水への浸漬の代わりに高温水素ガス（好適には３００～６００℃、圧力０．１～１ＭＰａ）に雰囲気内に１時間保持して行ったものを作製した。これらの水素吸蔵合金電極は上記実施例１～５の水素吸蔵合金電極とほぼ等しい容量利用率特性及び電池内圧特性を示した。この事実から還元処理に用いる還元剤は過酸化水素水に限定されないことがわかる。

【図面の簡単な説明】

【図１】実施例１の水素吸蔵合金電極の初期活性化特性を示す図である。

【図２】実施例１の水素吸蔵合金電極を用いた密閉電池の電池内圧特性を示す図である。

【図３】実施例３の水素吸蔵合金電極の初期活性化特性を示す図である。

【図４】実施例３の水素吸蔵合金電極を用いた密閉電池の電池内圧特性を示す図である。

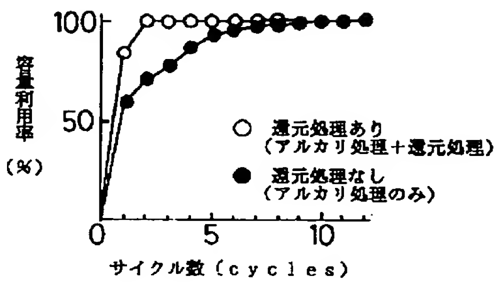
【図５】実施例５の水素吸蔵合金電極の初期活性化特性を示す図である。

【図６】実施例５の水素吸蔵合金電極を用いた密閉電池の電池内圧特性を示す図である。

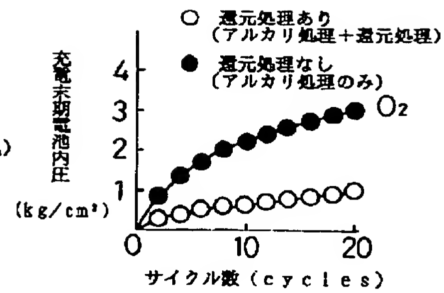
【図７】実施例７の水素吸蔵合金電極の初期活性化特性を示す図である。

【図８】実施例７の水素吸蔵合金電極を用いた密閉電池の電池内圧特性を示す図である。

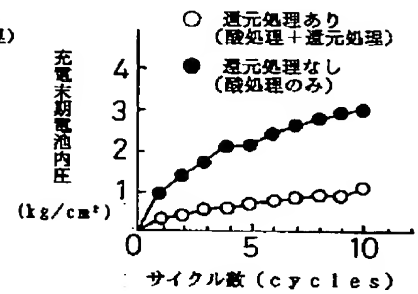
【図１】



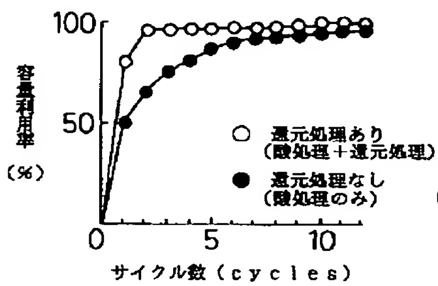
【図２】



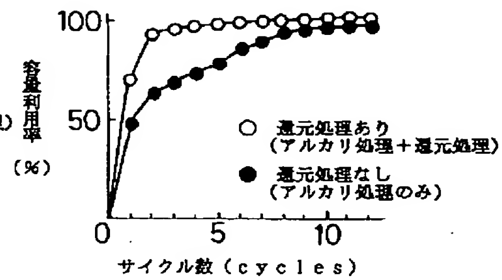
【図４】



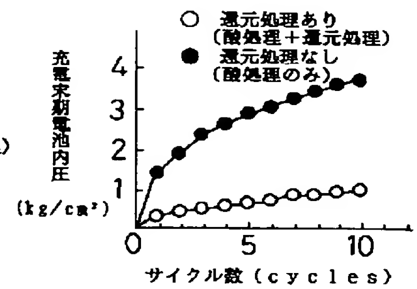
【図３】



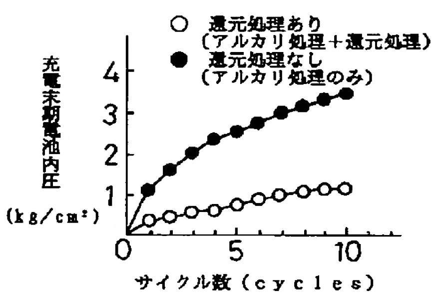
【図５】



【図８】



【図６】



【図７】